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B. T. GALLOWAY, *Chief of Bureau.*

THE RELATION OF THE COMPOSITION OF THE LEAF TO THE BURNING QUALITIES OF TOBACCO.

BY

WIGHTMAN W. GARNER,

SCIENTIFIC ASSISTANT, TOBACCO BREEDING INVESTIGATIONS,
BUREAU OF PLANT INDUSTRY.

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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF PLANT INDUSTRY,
OFFICE OF THE CHIEF,
Washington, D. C., April 13, 1907.

SIR: I have the honor to transmit herewith a manuscript entitled "The Relation of the Composition of the Leaf to the Burning Qualities of Tobacco," by Dr. Wightman W. Garner, Scientific Assistant in the Tobacco Breeding Investigations of this Bureau.

This paper contains much information of importance to growers, manufacturers, and tobacco breeders on points which have heretofore been very imperfectly understood. I would therefore recommend the publication of the manuscript as Bulletin No. 105 of the series of this Bureau.

Respectfully,

B. T. GALLOWAY,
Chief of Bureau.

Hon. JAMES WILSON,
Secretary of Agriculture.

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THE RELATION OF THE COMPOSITION OF THE LEAF TO THE BURNING QUALITIES OF TOBACCO.

INTRODUCTION.

Of the many requirements for a first-class smoking tobacco, whether for pipe or cigar, good burning qualities may be said to be most important. Not only are these essential in themselves, but the character of the combustion and the conditions under which it takes place constitute one of the principal factors which control the aroma. The widest variation is found among samples of tobacco as regards the burning qualities, and it frequently happens that an entire crop of the best quality in other respects is rendered almost valueless because it will not burn. The ultimate cause of this variation in burning qualities must be sought in differences in chemical composition. Experience has shown that the chemical composition of tobacco, as reflected in its burning qualities, is greatly influenced by the character of the soil, the climate, wet and dry seasons, and the kind of fertilizers applied to the soil. Moreover, there is good reason to believe that certain strains or types of tobacco possess the power of appropriating from the soil those constituents conducive to a good burn, while other closely related types under the same conditions are lacking in this power.

It is evident, therefore, that an accurate knowledge of the chemical characteristics of good and bad burning tobaccos is of fundamental importance in deciding upon the proper selection of soils and fertilizers in order to get the best results. It is highly probable also that such information would prove of great assistance in tobacco breeding in establishing strains possessing specially good burning qualities. Finally, it is well known that independently of the successful growing of a good tobacco crop the curing and fermentation are important factors in developing a good burn, and with a more complete knowledge of the chemical changes taking place in these processes further improvements in the methods now in use may be expected, for with better information as to the changes to be effected it will be much easier to develop the best methods for obtaining these results.

As applied to tobacco, the term "burning qualities" is a comprehensive one, including several different elements, chief of which are the fire-holding capacity, the evenness and completeness of the burn, and the character of the ash. The fire-holding capacity refers simply to the length of time the tobacco will continue to burn. Frequently samples of tobacco which possess a satisfactory fire-holding capacity show a tendency to carbonize, or "coal," in advance of the burning area and will not burn evenly. In some cases these defects appear to be due to injudicious combinations of the three component parts of the cigar, namely, the filler, the binder, and the wrapper; in other cases the cause lies in the chemical composition of the leaf. As to the quality of the ash, the important characteristics are the color and the firmness or cohesiveness. There is an essential difference between the combustion of most substances and the burning of tobacco. In the first case, the substance when ignited burns with a flame, and as soon as the flame is extinguished the combustion ceases. On the other hand, tobacco of good quality will not burn with a flame, but will continue to glow almost indefinitely.

It may be said in general that those substances which show the greatest tendency to burn with a flame have the least capacity for glowing, and vice versa, and this rule is applicable to different kinds of tobacco, for in cases of very rank growth where the leaf is thick and coarse or in any tobacco markedly deficient in mineral constituents there is a decided tendency to burn with a flame, whereas the capacity for glowing is lacking. The differences in the two kinds of combustion are well illustrated by the case of coal and its decomposition products when subjected to dry distillation. The volatile products, the larger portion of which goes to make up the illuminating gas, are inflammable, while the residual coke, consisting essentially of carbon, yields no flame when burned, but under favorable conditions will continue to glow until consumed. Now, in the burning cigar these two processes are both going on simultaneously and more or less independently of one another. The organic constituents of the leaf in the region immediately in advance of the burning area are undergoing the process of dry distillation, in which the volatile products for the most part escape and appear in the smoke. Moreover, it is this process which gives rise to the aroma. As the fire advances, the residue from the distillation, which consists of the mineral constituents of the tobacco, together with more or less carbon and stable organic condensation products, becomes incandescent, and the glow continues until practically all of the combustible matter is consumed, leaving as the final residue the ash. If certain of the mineral constituents of the tobacco which interfere with the combustion predominate, the resulting ash will be dark in color, while if

others which favor the complete combustion predominate, the ash will be white, or very nearly so.

From what has been said it is perhaps not surprising that the relation of the chemical composition to the burning qualities of tobacco early attracted the attention of agricultural chemists, and this problem has led to a large number of purely chemical investigations, as well as practical field experiments. But although more than fifty years have elapsed since the publication of the first important paper on the subject, by Schlösing, no one has as yet been able to offer a satisfactory explanation of the conduct of different kinds of tobacco as regards their burning qualities. Many theories have been put forward from time to time, but they have all proved to be either fundamentally erroneous or inadequate to explain all the facts. Except a few general relations which have been pretty fully established, the results obtained by different investigators have led to widely different and oftentimes contradictory conclusions. It will not be necessary to discuss or even mention here all the work which has been published on this important subject, and only those facts which seem to be best supported will be briefly reviewed.

In comparing the composition of the tobacco plant with that of other agricultural crops, the most striking characteristic is its remarkably high content of mineral matter, commonly spoken of as the ash. In some cases the ash content reaches 25 per cent of the total weight of the dry tobacco leaf, and the average is well above 15 per cent. For this reason by far the greater portion of the work of chemists on tobacco has been devoted to the study of the composition of this ash.

Broadly speaking, there are two methods of attacking the problem of the relation of the composition to the burn, one of which may be called the analytical and the other the synthetical. Nearly all of the investigations on this subject fall under the head of the analytical method, which consists simply in making comparative analyses of samples of tobacco having good and poor burning qualities, and attempting to trace the relation between the differences in composition and the good and bad burning qualities. An examination of the composition of a typical tobacco ash will show how extremely difficult it is to draw any positive conclusions from any set of analyses which will not be subsequently contradicted by other analyses.

In the first place, there are present in tobacco three inorganic acids and three bases, all of which occur in sufficient quantities to exert an important influence on the burn and all of which are subject to wide variations in quantity in different tobaccos. With such complex variations it is almost impossible to single out those differences which really exert determinative influences on the burn. But more impor-

tant still, with so many acids and bases present in the leaf, there is the possibility of very considerable differences in the distribution of the latter among the former, and in some cases these differences would certainly exert a very important influence on the burning qualities. It is quite impossible, however, to obtain any information as to the way in which the bases are distributed between the acids in different tobaccos by any available methods for the analysis of the ash. A very large number of analyses have been made of the ash of various sorts of tobacco grown in different parts of the world, but no one has been able to point out any constant relation between the varying quantities of the constituents of the ash and the differences in burning qualities.

It is to be regretted that in all these analyses no attempt has been made to distinguish between the sulphur existing in the plant as sulphate and that combined with organic compounds, although it has long been recognized that both forms are actually present, and in the case of some plants it has been found that the content of organic sulphur is much greater than that of sulphates. By the methods commonly used in the preparation of the ash for analysis, varying proportions of this organic sulphur are oxidized to sulphuric acid, while the remainder is lost; hence such analyses are valueless as a measure of the quantity of sulphate originally contained in the sample.

As opposed to the method of directly analyzing samples of tobacco with good and bad burning qualities, what may be called the "synthetical method" consists in determining the effect on the burn of adding to tobacco or some other suitable substance those compounds normally occurring in the leaf. It is difficult to get quantitative results in this way, but, on the other hand, positive results in a qualitative way can be obtained, which in the case of any one constituent added are largely independent of the effects of the other constituents. In this way conclusions are based on direct experiment and do not depend on the differentiation of several factors operating simultaneously and perhaps in opposite directions.

Schlösing[a] was the first investigator to study the problem by this method. He showed that the fire-holding capacity is not proportional to the amount of potassium nitrate, and concluded that potash in combination with organic acids is the principal factor favoring this property. If the potash is combined with sulphuric acid and chlorin and the organic acids are in combination with lime, a poor burn results; hence a tobacco with good burning qualities contains potash in excess of that equivalent to the sulphuric and hydrochloric acids. Schlösing attributed the beneficial action of the potash salts

[a] Landw. Vers. Stat., 3, 98.

of the organic acids to their peculiar property of swelling up to many times their original volume and thus yielding a porous mass of finely divided carbon when decomposed by heat.

Nessler[a] made a large number of experiments on the effects of various salts on the glowing capacity of filter paper, his method being simply to impregnate strips of the paper with solutions of the salts of definite strength. His principal conclusions are (1) that potash, especially in the form of sulphate and carbonate, acts very favorably on the fire-holding capacity, while lime and magnesia exert no marked effect except to whiten the ash; (2) that chlorids are very injurious, and (3) that potassium nitrate gives a quick but incomplete combustion, while calcium and magnesium nitrates act very favorably. Nessler admits that the organic potash salts favor the fire-holding capacity, but combats the theory of Schlösing in explanation of their favorable action. He points out that the ease with which these salts are decomposed by heat leads to carbonization, or "coaling," of the tobacco in advance of the burning area, which is a very undesirable property; and, moreover, that potassium sulphate, entirely lacking the property of swelling and yielding a carbonaceous residue when heated, also exerts a markedly beneficial influence on the fire-holding capacity. Nessler assumes that the favorable action of potash salts is due to the formation of a small amount of free potassium during the combustion, which serves as an energetic oxygen carrier; or, in other words, it is simply a catalytic action.

Mayer[b] has supplemented this work by including in his experiments many organic compounds, and concludes in general that these latter favor the burning with a flame, while they decrease the glowing capacity. The inorganic salts in general, especially those of potassium, favor the glowing capacity.

Nessler and Mayer based their conclusions on the supposition that the compounds tested would exert the same influence on tobacco as on filter paper, but this is by no means the case. The chief reason for this appears to be in the relative sensibility of filter paper and tobacco toward the salts affecting the glowing capacity. Filter paper, which is almost pure cellulose, is extremely sensitive toward metallic salts, and when moistened with a solution of any of the potash salts containing even as low as .25 per cent of potash will continue to glow indefinitely, while, on the other hand, ten times this quantity may entirely destroy this property. Tobacco contains, besides cellulose, many other organic substances which are far less combustible, and hence requires much larger quantities of these salts to produce appreciable effects on the burning qualities. For example, small quantities of potassium chlorid greatly improve the glowing capacity of

[a] Landw. Vers. Stat., 19, 309. [b] Landw. Vers. Stat., 38, 126.

filter paper, but when applied to tobacco in sufficient quantities to influence the burn the effect is very injurious. Conclusive results can not therefore be obtained by the use of filter paper alone; nevertheless they are of value as supplementing the test applied directly to the tobacco.

Dr. E. H. Jenkins[a] determined the amounts of potassium carbonate in the ash of a number of different types of tobacco, which is a rough measure of the quantities of organic potash salts originally present in the unburned tobaccos. No constant relation was found to exist between the amount of carbonate and the fire-holding capacity, and Jenkins concludes that the burning qualities are largely influenced by the organic constituents of the tobacco.

Van Bemmelen[b] maintains that the glowing capacity is governed by the relative quantities of alkali and of hydrochloric and sulphuric acids—expressed in chemical equivalents—in the tobacco. In good-burning samples the potash is largely in excess of the acids, while in the bad-burning samples the acids are equal to or in excess of the alkali. Apparent exceptions to this rule are explained by the assumption that the potash may be partly replaced by lime and magnesia. This theory appears to be the nearest approach to the true explanation of the cause of the good and bad burning qualities of tobacco of any yet offered, but the assumption that the favorable influence of the potash on the burn may be also exerted to any considerable extent by lime and magnesia under certain conditions is contrary to the evidence bearing on this point.

Fesca,[c] from his studies of Japanese tobacco, concludes that chlorin and sulphur have a very unfavorable influence on the burn, but phosphorus is indifferent.

Barths[d] agrees in general with the conclusions reached by Nessler and Mayer, and believes that the beneficial effect of potash salts are produced by the reduction of the potash compounds to potassium oxid and free potassium, which serve as energetic oxygen carriers, as was suggested by Nessler. The injurious effects of certain inorganic salts are due either to their nonreducibility or to their easy fusibility. The alkali phosphates are regarded as particularly injurious because of their easy fusibility.

Summarizing the results obtained by the investigators mentioned, it is evident that the only two facts which have not been disputed are (1) that chlorin injures the fire-holding capacity and (2) that potash favors this property.

The effects of sulphates and phosphates and the relative value of the different salts of potash in promoting the fire-holding capacity

[a] Ann. Rpt. Conn. Agr. Expt. Sta., 1884, p. 96.
[b] Landw. Vers. Stat., 37, 409.
[c] Landw. Jahrb., 1888, 329.
[d] Landw. Vers. Stat., 39, 81.

are disputed points. The same is true also of the effects of lime and magnesia on the burning qualities. The two facts which have not been contradicted are insufficient in themselves to explain the burning qualities of different samples of tobacco, for it rarely happens that tobacco contains enough chlorin to produce any injurious effects, and it frequently happens that samples very rich in potash have a poor burn, while others comparatively poor in this constituent show excellent burning qualities.

It seemed quite possible that some further light might be thrown on the subject by extracting different samples of tobacco with various solvents and noting the effect on the burning qualities. It should be stated here that all samples of tobacco used in the experiments described in this paper had been thoroughly fermented, and the results are not intended to be applied to unfermented tobacco. Extraction of various samples with petroleum ether and with ordinary ethyl or sulphuric ether did not appreciably affect the burning qualities. When strong alcohol was used as the solvent the same result was obtained, except in a single case, where the fire-holding capacity was considerably improved by the extraction.

More striking results are obtained when tobacco is extracted with water. The following simple experiment is very interesting and instructive: A leaf of tobacco having a good glowing capacity is divided along the midrib into two parts; one of which is extracted for forty-eight hours with a comparatively large volume of distilled water. After being dried the extracted portion of the leaf will be found to have entirely lost its glowing capacity. Now, if the extract be evaporated down to a very small volume and a bit of the extracted leaf saturated therewith and dried, it will once more show a good fire-holding capacity. Whether this is less or greater than the original leaf possessed will depend, of course, on the concentration of the extract. This extract will further impart a good burn to filter paper and to other samples of tobacco showing poor burning qualities. This simple experiment seems to prove conclusively that the active principle or principles in imparting to the tobacco leaf its capacity for holding fire can be extracted with water.

The problem, then, is to determine the composition of the extract and to discover which of its constituents contribute to the burning qualities of the tobacco. One hundred grams of tobacco having a good burn were extracted with 1 liter of distilled water; the extract was poured off and the tobacco again extracted with the same quantity of water for twenty-four hours longer. The extracts thus obtained were combined, filtered, and evaporated to about 150 c. c. During the evaporation a considerable quantity of calcium citrate separated out, which was removed by filtration. The filtrate was

made up to 200 c. c. and aliquot portions were taken for analyses. The principal constituents of the extract are the chlorid, sulphate, nitrate, citrate, and malate of potassium, together with ammonium and nicotine salts and small quantities of lime and magnesia. For comparison, the ash of the extracted tobacco was also examined and it was found that practically all of the phosphoric acid, about one-half of the magnesia, all of the oxalic acid, and the greater portion of the lime remain in the leaf, while the extract contains nearly all the chlorin, all the potash, malic, citric, and nitric acids, and most of the sulphuric acid. About one-half of the total ash is extracted from the leaf by this process, and this seems to contain all the constituents which impart to the tobacco the capacity for holding fire.

An extract of a tobacco having poor burning qualities was prepared in the same way, and it also showed the power to impart the capacity for holding fire, but as nearly as could be measured this power was only about one-fifth of that shown by the extract from the tobacco having good burning qualities. It differed from the latter as regards composition in that it contained about five times as much sulphuric acid, twice as much magnesia, and considerably less nitric acid. The total quantity of potash was about the same in the two extracts, so that the extract from the tobacco with poor burning qualities contained much less potash in combination with the organic acids. The difference in composition of these extracts, then, obtained from tobaccos having good and bad burning qualities, indicates that the principal factor favoring the burn is the potash in excess of the amount required for combining with the mineral acids.

EFFECTS OF THE VARIOUS CONSTITUENTS OF THE ASH ON THE BURNING QUALITIES OF TOBACCO.

The experiments previously described show conclusively that those compounds which are most important in promoting the burn of tobacco can be removed by extraction with water; but the water extract is a complex mixture of salts, and it is therefore desirable to determine the relative effects of each of these constituents. In order to do this, solutions of certain definite strength were prepared of all of the salts which are found in the extract, and the effects of all these on the burning qualities of various samples of tobacco when applied singly or in combination were noted. In testing the effects of any one base combined with the different acids the solutions were all made of such strength that the quantity of the basic element was always the same, regardless of the molecular weights of the salts used in the experiments. The salt solutions were applied to small strips of the leaf, either by placing them in a watch glass and pouring over them a quantity of the solution to be tested just sufficient to thor-

oughly saturate them, thus avoiding any leaching out of the soluble constituents of the leaf, or by spraying the strips and allowing them to stand in a moist atmosphere until the solution had diffused through the leaf. In every case a strip of the leaf adjoining the portion treated with the solution was reserved for comparison. The tests on different samples of tobacco did not always agree, as was to be expected, since the quantities of the various salts already present in the leaf are subject to wide variation, and these differences in some cases may overshadow the effects of the salt added. For the same reason the concentration of the solution added must be taken into account. To overcome these factors it is necessary to apply each test to a number of different samples of tobacco. The tests on tobacco were always further supplemented with similar experiments on strips of filter paper.

There are three base-forming elements which occur in tobacco in sufficient quantities to require consideration—potassium, calcium, and magnesium—while the important mineral acids are sulphuric, phosphoric, hydrochloric, and nitric, and the chief organic acids are citric, malic, and oxalic. Little is known of the actual distribution of the three bases among the acids and so it is necessary to test all of the possible combinations. It is probable, however, that the sulphuric, nitric, and hydrochloric acids are for the most part combined with potash so far as the quantity of this base present will suffice to neutralize these acids and that any excess of potash would be in combination with the organic acids. All of the oxalic acid appears to be combined with lime. If the acids and bases were allowed to interact in the presence of water, the distribution of the latter among the former would be controlled simply by the relative solubilities of the resulting salts and the strengths of the acids and bases; but during the life processes of the plant, which do not cease until some time after the tobacco has been placed in the curing shed, other forces come into play, and it hardly seems probable that there is sufficient water left in the leaf after the life activities have ceased to permit of a readjustment between the acids and bases according to purely chemical forces.

POTASSIUM.

All the salts of potassium are soluble, so that there is no difficulty in testing the salts at any desired concentration. Those most used for applying the tests to tobacco contained 1 per cent and 2 per cent, respectively, of potassium, while for tests with filter paper much weaker solutions gave the best results. In the case of the chlorid it was found that the addition of comparatively large quantities practically destroyed the burning qualities of tobacco, while moderate amounts caused very incomplete combustion, leaving a heavy black

residue. While chlorin is undoubtedly injurious, these experiments all indicated that it requires larger quantities to seriously affect the burning qualities than is commonly supposed. The sulphate, when added in any considerable quantity, invariably injured the burning qualities very markedly, acting in this respect very much like the chlorid but to a lesser degree. The conclusion reached by Nessler that potassium sulphate is highly beneficial, which was based on experiments with filter paper, is thus shown to be erroneous. Potassium nitrate in large quantities causes tobacco to burn explosively and the combustion is incomplete; in smaller quantities it exerts a distinctively beneficial action, but not more so than some other potash salts. The quantity of potash combined with nitric acid in tobacco is generally comparatively small, and other forms of potash are more important in promoting the fire-holding capacity. As regards the phosphates, only the dipotassium salt need be considered, and this appears to be practically neutral in its action, neither promoting nor hindering the fire-holding capacity. Moreover, as compared with the other important acids the quantity of phosphoric acid is nearly always small. The oxalate, citrate, malate, and acetate of potash all showed very beneficial effects in every case, though much larger quantities were required for some samples of tobacco than for others. Excessive amounts of these salts, on the other hand, injured the burning qualities, especially as regards the character of the ash. Also when applied to filter paper in small quantities, the latter acquires a good fire-holding capacity, whereas large amounts again destroy this property. The acetate is considerably less efficient in improving the fire-holding capacity than the other three organic salts, probably on account of its greater stability.

CALCIUM.

Considerable difficulty is met with in getting accurate tests with the calcium salts because nearly all of them are difficultly soluble, and hence solutions can not be obtained of sufficient strength to give decided results. Only the chlorid, nitrate, and acetate are easily soluble, and of these the nitrate shows an anomalous conduct, and so the results obtained with this salt are not specially significant. In the case of the insoluble salts, emulsions were applied to the tobacco, but of course results obtained in this way are not as reliable as those secured by use of solutions. The chlorid of calcium is very injurious to the fire-holding capacity and decidedly more so than the potassium salt, so that even small quantities destroy this property. Calcium sulphate in moderate quantities injures the burn markedly and to a greater extent than the corresponding potassium salt. The effect of the nitrate of calcium on the burn is somewhat surprising. If a

sample of tobacco with good burning qualities is saturated with a 10 per cent solution of the nitrate and dried, it burns with extreme rapidity, almost explosively, and gives a remarkably white ash, while with samples of tobacco with poor burning qualities scarcely any beneficial effects are produced. More dilute solutions, such as were used in the case of the other salts, do not produce any appreciable effects. Moreover, it requires a concentrated solution to impart to filter paper a good fire-holding capacity. It seems likely that the effects of the concentrated solution on the tobacco with the good burning qualities are due largely to reaction of the calcium nitrate with potash salts in the leaf. So far as could be determined no marked effects are produced by adding calcium phosphate to tobacco. The acetate of calcium is of special interest because it is readily soluble and thus furnishes an opportunity of comparing the relative effects of potassium, calcium, and magnesium on the burning qualities. Of a large number of samples of tobacco tested a few were improved by the acetate, but the greater number were scarcely affected as regards the capacity for holding fire. In every case, however, the color of the ash was very materially improved. None of the remaining salts of calcium to be considered are easily soluble, but so far as could be determined they neither injure nor improve the fire-holding capacity to any considerable extent, but all give a decidedly whiter ash.

MAGNESIUM.

All the salts of magnesium are readily soluble except the phosphates, and so it is much easier to get satisfactory results with them than is the case with the calcium compounds. The chlorid and sulphate are both very decidedly injurious to the burn, and the addition of even small quantities will destroy the glowing capacity of tobacco having the very best burning qualities. The sulphate is much more injurious than the corresponding calcium salt. The nitrate acts very much like the calcium compound, but its action when applied in concentrated solution is less marked. When applied to filter paper it shows the peculiar property of charring the paper in wave-like forms much in advance of the burning portion. The phosphate of magnesium appears to be more injurious to the burn than the corresponding calcium compound. The acetate was found to injure the burning qualities in every case, but to a lesser extent than the inorganic salts. The citrate, malate, and oxalate in a few cases did not interfere with the burn, but in the greater number harmful effects were observed. All of the salts of magnesium, like those of calcium, tend to produce a white ash.

MINERAL AND ORGANIC ACIDS.

In describing the results of the tests with the various salts these have been grouped under the heads of the three bases, potassium, calcium, and magnesium, but it is also instructive to consider them arranged according to the acids with which these bases are combined.

Chlorids.—All of the chlorids injure the burn, but that of potassium much less than the calcium and magnesium salts.

Sulphates.—All of the sulphates injure the fire-holding capacity, but to very different degrees. The potash salt is decidedly less harmful than that of calcium, while the magnesium compound is remarkably injurious, being comparable with the chlorids in this respect.

Nitrates.—The potash salt is very favorable to the burn, but the calcium and magnesium compounds produce little effect except when present in very large quantities.

Phosphates.—Dipotassium phosphate is practically neutral in its effect, while the calcium and magnesium salts are somewhat harmful.

Salts of organic acids.—The potassium salts are very favorable to the burn, the calcium salts are slightly beneficial, and the magnesium salts are somewhat injurious.

It would seem from these results that the effect on the fire-holding capacity of any element entering into the composition of the ash depends more on the nature of its combination than on the quantity which is present. In the case of sulphuric acid, for example, a considerable quantity combined with potash would not seriously injure the glowing capacity, while even a small amount of it in combination with magnesium would entirely destroy this property. Again, the organic acids when combined with potash are very beneficial, but in combination with magnesia their favorable influence entirely disappears.

It is evident that the one element on which the fire-holding capacity is entirely dependent is potassium. But it is equally essential that part of the potash be in combination with organic acids, for it is to this form chiefly that its beneficial action is due. The nitrate of potash when present in considerable amounts undoubtedly contributes also to this property. Schlösing, as has been said, attributed the beneficial effects of the organic potassium salts to the peculiar property which they possess of swelling up to many times the original volume when decomposed by heat, thus leaving a very porous, finely divided residue of carbon, which continues to glow until combustion is complete. This explanation, however, is inadequate, for there are other salts which promote the glowing capacity but do not yield the carbonaceous residue when heated.

It will be observed that all the potash salts which favor the property of glowing, including the nitrate, yield in the combustion the

carbonate. It was found, in fact, that the carbonate itself is just as efficient in imparting the property of glowing to tobacco as the organic salts, and the same is true of the bicarbonate. This fact points strongly to the conclusion that the favorable action of the potash salts is dependent on the ease with which they yield the carbonate. It seems possible that the carbonate or bicarbonate by alternately giving off and taking up carbon dioxid may serve as a means of removing this gas at the most favorable moment, the effect being somewhat the same as when nitrates render organic substances combustible by supplying oxygen in a highly concentrated state. It may be, however, that the potassium oxid formed from the carbonate is further reduced to the metallic state by the highly heated carbon, thus serving as an energetic oxygen carrier, as was suggested by Nessler. Whatever may be the peculiar properties of these potash salts which give them the power of imparting the property of glowing to tobacco, it is certain that these properties are not shared by the salts of calcium and magnesium except to a very limited degree.

While the inorganic salts of calcium are injurious to the fire-holding capacity, the compounds of this base considered collectively may be said to be inert with reference to this quality. The compounds of magnesium are all injurious, but the harmful effects are greatly reduced when the magnesium occurs in combination with the organic acids.

The question has often been raised whether lime and magnesia may not, in part at least, replace potash without injuring the burning qualities. Many ash analyses which have been made seem to indicate that this is the case, while others point to the opposite view. This assumption is made by Van Bemmelen [a] to explain the fact that in some samples of tobacco which show a good fire-holding capacity the total quantity of potash is only very slightly in excess of that necessary to neutralize the sulphuric and hydrochloric acids. But Van Bemmelen's calculations are all based on the ash analyses, and it has been pointed out that the estimation of the sulphuric acid in the ash gives no indication of the quantity of sulphur actually present in the tobacco in the form of sulphates and therefore that the amount of potash in organic form may be considerably greater than calculations based on these data would indicate.

In so far as lime alone is concerned the conclusion to be drawn from our experiments is that this can only replace part of the potash when the latter is present in combination with organic acids in quantities larger than are necessary to produce a good burn; for while organic salts of lime do not appear to injure the fire-holding capacity, they do not specially favor it. The amount of potash in organic form

[a] Landw. Vers. Stat., 37, 409.

necessary to impart the property of glowing to tobacco no doubt is influenced to some extent by variations in the other organic constituents of the leaf, but our experiments have shown that excessive quantities of these salts tend to injure the burn by causing a too rapid combustion. It may happen, therefore, that a sample of tobacco contains more organic potash than is necessary to produce the best burn, and in such cases a portion of it could be replaced to advantage by lime. Since magnesia compounds as a whole tend to injure the burn it seems certain that the replacement of potash to any considerable extent by this element would seriously injure the burning properties.

For purposes of experimentation looking to the production of tobaccos possessing superior burning qualities, either by means of fertilizers and improved methods of curing and fermentation or by breeding and selection, it is very desirable to have at hand some method of testing the results by chemical examination. This is especially true because of the complexity of conditions which influence the qualities of tobacco. For example, if the attempt is made to improve the burning qualities by the use of certain potash salts, with a view to increasing the amount of potash in organic form in the tobacco, the result of the experiment may be entirely obscured by extraneous factors, such as improper curing and fermentation, if the fire-holding capacity alone were determined. Of course, in this particular case chemical analysis would reveal whether the object sought had really been attained, but there are other questions of chemical composition pertaining to this problem which can only be measured with difficulty by the methods at present available. This is especially true of the manner in which the bases are distributed among the acids in tobacco and whether this distribution is essentially different in different samples.

All of the important organic acids, and also nitric acid, when combined with potash seem to be about equally efficient in promoting the fire-holding capacity. Oxalic acid, however, is probably always combined with lime and so it is of little value in this connection. Since a portion at least of the potash combined with organic acids, as well as that present in the form of nitrate, will appear in the ash of the tobacco as carbonate, the determination of this latter quantity gives a rough measure of the amount of these salts originally present and is therefore by far the most important single criterion for judging the burning qualities in a chemical way.

We have tested a number of samples of tobacco grown in Connecticut in this way, in each case using one half of the leaf for testing the alkalinity of the ash and the second half for finding the fire-

holding capacity. To obtain some indication as to whether lime and magnesia can partly replace the organic potash, the alkalinity of the ash due to these bases was also determined, but the evidence on this point was all of a negative character, for the alkalinity due to lime and magnesia collectively did not show any apparent relation to the glowing capacity. In the case of the alkalinity due to potash—that is, the quantity of the potassium carbonate—however, there is unmistakable evidence of a close relation between these values and the capacity for holding fire, and if the method were really a true measure of the organic potash it is believed that there would be very few, if any, exceptions to this rule.

The samples used for this test were selected with special reference to the tobacco-breeding experiments which are being carried on by the Bureau of Plant Industry, and were taken from crops produced from the seed of individual selections of four different types of tobacco originally found growing in the same field. Both the light and the dark wrappers were examined in each case, and in every instance the former as compared with the latter showed a much greater fire-holding capacity and a much higher percentage of potassium carbonate in the ash. Also as regards the same grade of leaf of the different strains of each type, as well as of the different types taken collectively, the potash alkalinity was found to be directly proportional in nearly every case to the capacity for holding fire. This was especially true of the different strains of any one type. These tobaccos were all grown under as uniform conditions as could be obtained with reference to soil and fertilizers, and the results make it very probable that certain types or strains of tobacco possess the power of appropriating potash in forms favorable to the burning qualities to a greater degree than others growing under the same conditions, though further data are required to fully prove this point. The question is certainly a very important one from the standpoint of practical tobacco breeding and is worthy of very careful study.

THE CHARACTER OF THE ASH.

A tobacco with satisfactory burning qualities besides having the necessary capacity for holding fire must also yield a good ash. Although the organic potassium salts greatly favor the fire-holding capacity, they tend to produce a mottled, dark-colored ash. This is no doubt due to the easy fusibility of the alkali carbonate, which in melting incloses very small particles of unburned carbon and thus prevents complete combustion. Moreover, these salts when present in considerable quantity show a tendency to cause the tobacco to "coal" or carbonize in advance of the glowing portion, because they decompose so readily when heated.

The fact that the calcium and magnesium salts produce a white ash has already been mentioned, and at least one of these is essential to this property. On the other hand, tobacco containing excessive amounts of lime gives an ash which, although it is very light in color, lacks cohesion, or, in the language of the trade, it "flakes." This is a very objectionable property and must always be taken into account in judging the burning qualities of tobacco. The potash salts, more especially the organic compounds, yield an ash which is firm and compact but dark in color. From these facts, then, it is clear that potash and lime combined in the proper proportion are essential to a firm, light-colored ash. There is no apparent reason to suppose that magnesia is of any special significance in this connection further than the fact that it acts like lime.

THE RELATION OF THE ORGANIC CONSTITUENTS TO THE BURNING QUALITIES.

The organic compounds constitute the material which is consumed in the combustion of the tobacco, and in some way the mineral constituents, more particularly the potash salts, impart to this material the property of burning without flame. If the mineral constituents are extracted from a leaf of tobacco, it will then only burn with a flame, the glowing capacity having been entirely lost. However, some of the organic compounds show a greater tendency to burn with a flame than do others, and hence act less favorably on the glowing capacity, for, as has been stated, these two qualities usually stand in inverse ratio to one another. The principal compounds or classes of compounds which need to be considered in this connection are cellulose, the organic acids, pectin, the so-called tobacco tars, plant wax, the sugars, nicotine, and other organic nitrogenous compounds. For the purpose of studying the composition of the leaf with reference to its burning qualities we may consider cellulose, which constitutes from 10 to 15 per cent of the total weight, as the fundamental or basic material, which receives its capacity for glowing from certain mineral salts. Pure cellulose in the form of filter paper is exceedingly sensitive to the catalytic action of these mineral salts, very small quantities of them being sufficient to cause the paper to burn without flame indefinitely, but when the other organic constituents of tobacco are present this sensibility is greatly affected and much larger quantities of the catalytic agent are necessary to produce a good fire-holding capacity. Cellulose, then, must be considered as a very favorable factor in promoting this property of holding fire.

There are a large number of organic acids normally occurring in tobacco, but of some of these practically nothing is known. Atten-

tion has been called to the fact that citric, malic, oxalic, and acetic acids in combination with potash exert a very favorable influence on the burning qualities. It was found by direct experiment that these acids in the free state injure these qualities, but as they probably never occur free in fermented tobacco this fact is of little consequence. Citric and malic acids are undoubtedly of fundamental importance in producing good burning qualities, but since oxalic acid occurs in combination with lime and not with potash in tobacco it is of little value in this respect. Pectin and the pectoses are present in considerable quantities in cured tobacco leaves, but, according to Schlösing, these are all converted into pectic acid during the process of fermentation. A sample of pectic acid prepared from fermented tobacco was found to produce no injury to the fire-holding capacity; in fact, when combined with potash it acted favorably on this property.

According to Kissling, the tobacco tars, consisting of a mixture of a number of chemical individuals, exert an important influence on the quality of the product. Some of these are of an acid character, while others are indifferent substances. When tobacco is extracted with large volumes of water, as previously described, considerable quantities of these tarry acids combined with nicotine and other bases pass into solution, and on evaporation of the extract the salts are decomposed, the nicotine volatilizing and the tarry acids being precipitated. These acids in the free state were found to be decidedly injurious to the burning qualities, but they occur in tobacco in comparatively small quantities.

A number of samples of tobacco of very poor burning quality were extracted with alcohol to determine if this solvent would remove any constituents deleterious to the burn, but with the exception of a single case this treatment did not improve the tobacco in this respect. The constituents removed by extraction with alcohol are nicotine combined with acids, tannic acid, glucosides, sugars, and the tars and tarry acids; hence it appears that none of these compounds are of special importance with reference to the burn. Direct experiments showed that glucose does not materially influence the burning qualities. Nicotine is the characteristic alkaloid of tobacco and is of great importance with reference to its physiological action, but its salts were found to have no effect on the burn. In addition to nicotine the important nitrogenous constituents are the amido compounds and the albuminoids. It is generally believed that the amido compounds exert a favorable and the albuminoids an unfavorable influence on the desirable qualities of tobacco, including the burn, although there is little experimental proof of this theory. The quantity of plant wax occurring in tobacco is too small to affect the burning qualities.

SUMMARY.

The principal facts brought out by the experiments which have been described on the relation of the chemical composition to the burning qualities of tobacco may be briefly summarized in the following general statements:

(1) The fire-holding capacity is dependent primarily on the content of potash combined with organic acids.

(2) Lime in general does not greatly affect the fire-holding capacity, but is an essential factor in the production of a good ash.

(3) Large amounts of magnesia tend to injure the capacity for holding fire.

(4) Chlorin injures the burning qualities, but it seldom happens that tobacco contains enough of this element to do any serious harm.

(5) Sulphates in general injure the burning qualities, but the effects are not so marked when all the sulphuric acid is combined with potash.

(6) So far as is known none of the organic constituents of tobacco, with the possible exception of the so-called tarry acids and the albuminoids, exert a very important influence on the burning qualities.

From these conclusions it appears that the principal objects to be attained in efforts to improve the burning qualities of tobacco by breeding and by improved methods of production, especially in the use of the proper fertilizers, are (1) a relatively high content of potash combined with citric and malic acids, with a minimum amount of inorganic salts, especially chlorids and sulphates; (2) a moderate content of lime; (3) a comparatively small percentage of magnesia. and (4) a low content of organic nitrogenous compounds, more especially the albuminoids or proteids. Of these problems the first mentioned is altogether the most important from a practical standpoint and also the most difficult to solve. It has long been known that the muriate can not be used as a source of potash in the production of tobacco which is intended for smoking purposes, because of the injurious effects of the chlorin. The other available sources of potash at the present time are the sulphate, the carbonate, and the silicate.

Schlösing,[a] in his experiments with the use of the sulphate as a fertilizer for tobacco, found that the potash is assimilated, while the content of sulphuric acid is not increased. Jenkins,[b] on the other hand, in experiments conducted at the Connecticut Agricultural Experiment Station and extending over a period of several years, has shown that the composition of tobacco ash is profoundly modified by the use of different forms of potash and that applications of

[a] Landw. Vers. Stat., 3, 98.

[b] Ann. Rpt. Conn. Agr. Expt. Sta., 1896.

the sulphate greatly increase the quantity of sulphuric acid in the ash. The carbonate would seem to be an ideal form in which to supply the potash for combining with the organic acids in the plant, and its use has generally been found to improve the burning qualities. But, aside from the high cost of this material, there are other serious objections to its use, for it has a very strong alkaline reaction, and it seems probable that when used in large quantities it will eventually injure seriously the productiveness of the soil. The silicate is free from these objectionable properties, and if the potash can be made available there is every reason to believe that this will prove to be a very valuable source of potash for tobacco.

The sum of the lime and the magnesia in tobacco does not, as a rule, vary widely; or, in other words, the greater the amount of lime the less will be the amount of magnesia, and vice versa. The application of fertilizers containing magnesia increases the percentage of this element in the tobacco, but when used in the form of the carbonate the injury to the burning qualities would be reduced to a minimum. It is believed, however, that the use of fertilizer salts containing magnesia in the form of sulphate is inadvisable.

The percentage of organic nitrogenous compounds, including nicotine, is generally proportional to the luxuriance and vigor of growth; hence tobacco of very rank growth contains excessive quantities of these constituents. Again, these substances are most abundant when the plant is, as a whole, growing most rapidly, and also in the most rapidly growing parts of the plant. Conditions favorable to rank growth are brought about by the use of excessive quantities of nitrogenous fertilizers, especially when the nitrogen is in readily available forms. The chief danger from this source, however, lies in the application of quickly available forms of nitrogen during the later stages of growth, thus preventing or delaying the normal ripening of the leaf. Since the percentage of albuminoids decreases rapidly throughout the ripening process after the leaf has reached its full growth, this is an important reason why tobacco should not be harvested until the leaf is well ripened.

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